

## Short range order in new rock salt type structures of the system $\text{Li}_3\text{NbO}_4\text{-CoO}$

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Recibido el 12 de noviembre de 2004; aceptado el 14 de marzo de 2005

Synthesis of compounds belonging to the system  $\text{Li}_3\text{NbO}_4\text{-CoO}$  has been obtained by a solid state reaction, the products are appropriately described by the formula  $\text{Li}_{(3-3x)}\text{Co}_{4x}\text{Nb}_{(1-x)}\text{O}_4$ ;  $0 \leq x \leq 1$ . These new compounds have been studied in their diffraction features. Their electron diffraction patterns are characterized by the existence of a well defined diffuse intensity distribution in addition to sharp Bragg reflections of a rock salt type structure. This has been attributed to the presence of atomic short range order in the structure. As the amount of  $\text{Co}^{2+}$  ions increases in the structure, the amount of grains which produces diffuse scattering becomes larger therefore, we propose that the presence of  $\text{Co}^{2+}$  drives local spatial cation distribution which would rise electron diffuse scattering. An explanation, in terms of a modulated structure, has been put in advance depicting a probable atomic arrangement to explain the detected short range order.

*Keywords:* Electron diffraction; diffuse scattering; short range order; lithium cobalt niobium oxides.

En el sistema  $\text{Li}_3\text{NbO}_4\text{-CoO}$  se obtuvieron diversos compuestos mediante síntesis por estado sólido; los productos se describen de manera apropiada por la fórmula  $\text{Li}_{(3-3x)}\text{Co}_{4x}\text{Nb}_{(1-x)}\text{O}_4$ ;  $0 \leq x \leq 1$ . Las características de difracción de estos nuevos compuestos fueron estudiadas. Sus patrones de difracción electrónica están caracterizados por la existencia de una distribución de intensidad difusa bien definida, en adición a los intensos puntos de reflexión de Bragg de una estructura tipo sal de roca. Esto se atribuye a la presencia de orden atómico de corto alcance en la estructura. Conforme la cantidad de iones  $\text{Co}^{2+}$  se incrementa en la estructura, la cantidad de granos que producen dispersión difusa es mayor, por lo que se propone que la presencia de iones  $\text{Co}^{2+}$  favorece una distribución espacial local de cationes la cual produce dispersión difusa de electrones. Se propone una explicación en términos de una estructura modulada con un probable arreglo atómico para explicar el orden de corto alcance detectado.

*Descriptores:* Difracción electrónica; dispersión difusa; orden local; óxidos de litio, cobalto y litio.

PACS: 81.05.Je

### 1. Introduction

Using electron diffraction techniques, we have recently observed [1] the occurrence of diffuse scattering in electron diffraction patterns of some compounds from the join  $\text{Li}_2\text{SnO}_3\text{-CoO}$ , which belongs to the systems  $\text{Li}_2\text{SnO}_3\text{-MO}$ , where  $\text{M}^{2+}=\text{Mn}$ ,  $\text{Mg}$ ,  $\text{Co}$ ,  $\text{Cu}$ ,  $\text{Ni}$ , and  $\text{Zn}$  [2,3]. Three-dimensional distribution of diffuse scattering in the reciprocal space is caused by the presence of short range order in microscopic regions in real space of a crystal lattice [4]. So, when observed on the screen of the electron microscope or on a photography, the corresponding diffraction patterns show different sharp intensity contours as the crystalline orientation changes.

In the system  $\text{Li}_2\text{SnO}_3\text{-CoO}$ , with general formula  $\text{Li}_{2(1-x)}\text{Sn}_{(1-x)}\text{Co}_x\text{O}_3$  and, compounds which have NaCl type structure, we used octahedral polyhedra of ions regularly arranged in space to propose a probable cation distribu-

tion which could rise the observed diffuse scattering. Then, we followed the model by Sauvage and Parthè [5], whose main characteristic is a generalization of the Pauling's electrostatic valence rule. When using polyhedra of ions regularly arranged in space to describe derivative structures, the relations amongst short range order parameters may arise if the smallest building blocks of the structure have, as far as possible, an identical composition with the overall composition of the compound.

There are large amount of reports in the literature about short range order in alloys, oxides, carbides, and other crystalline structures. For example, in rocksalt type structures such as  $\text{Ti-O}$  [6] or in  $\text{VC}_{1-x}$  [7], the origin of diffuse scattering involves vacancy ordering.

In the present work, we have studied several new compounds of the system  $\text{Li}_3\text{NbO}_4\text{-CoO}$ , whose binary diagram was elaborated [8]. Results exhibit quite interesting features. Concerning this point, we want to discuss electron diffraction

results obtained from experiments performed in several of the prepared compounds. In this study, the results resemble those from  $\text{Li}_2\text{SnO}_3\text{-CoO}$ , especially the presence of diffuse scattering, as it will be described here.

## 2. Experimental

Samples of the system  $\text{Li}_3\text{NbO}_4\text{-CoO}$  were prepared through an solid state reaction. The phase  $\text{Li}_3\text{NbO}_4$  was firstly prepared by reacting mixtures of  $\text{Li}_2\text{CO}_3$  (Aldrich 99.9% purity) with  $\text{Nb}_2\text{O}_5$  (Aldrich 99.5% purity). Using Au foil, mixtures were reacted in an electric furnace; they were kept initially at  $650^\circ\text{C}$  for two days to drive off  $\text{CO}_2$ , and then at  $850^\circ\text{C}$  for two days (in air) to complete the reaction. Stoichiometric mixtures of  $\text{Li}_3\text{NbO}_4$  and  $\text{CoO}$  (Aldrich 99.99%) were prepared in Pt crucibles at different temperatures in a nitrogen atmosphere. Products and crystallinity were controlled by X-ray powder diffraction with a Siemens D5000 diffractometer, and  $\text{Cu } K_{\alpha 1}$  radiation.

Electron diffraction experiments were performed in fresh samples by crushing the powdered reaction products under alcohol and then dropping the suspension on a Cu grid covered with a hole carbon film.

Samples were examined in a Jeol 1200B electron microscope, operated at 100 and 120 keV.

## 3. Results and discussion

In the system  $\text{Li}_3\text{NbO}_4\text{-CoO}$ , the general formula which describes all obtained compounds is  $\text{Li}_{(3-3x)}\text{Co}_{4x}\text{Nb}_{(1-x)}\text{O}_4$ ;  $0 < x < 1$ , at  $1200^\circ\text{C}$ . Results of the electron microscopy study will be described by selecting different composition intervals of the phase diagram.

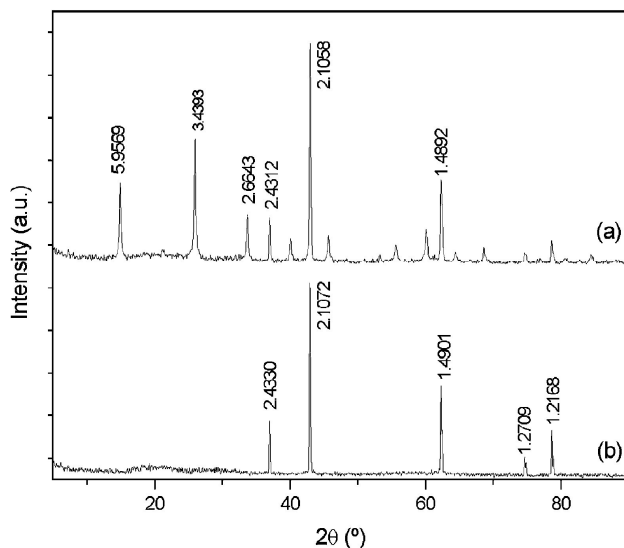


FIGURE 1. Typical X ray powder diffraction pattern of the phases (a) solid solution of  $\text{Li}_3\text{NbO}_4$  in the composition region  $0 < x \leq 0.143$ , and (b) solid solution of  $\text{CoO}$  in the composition region  $0.077 \leq x \leq 0.272$ .

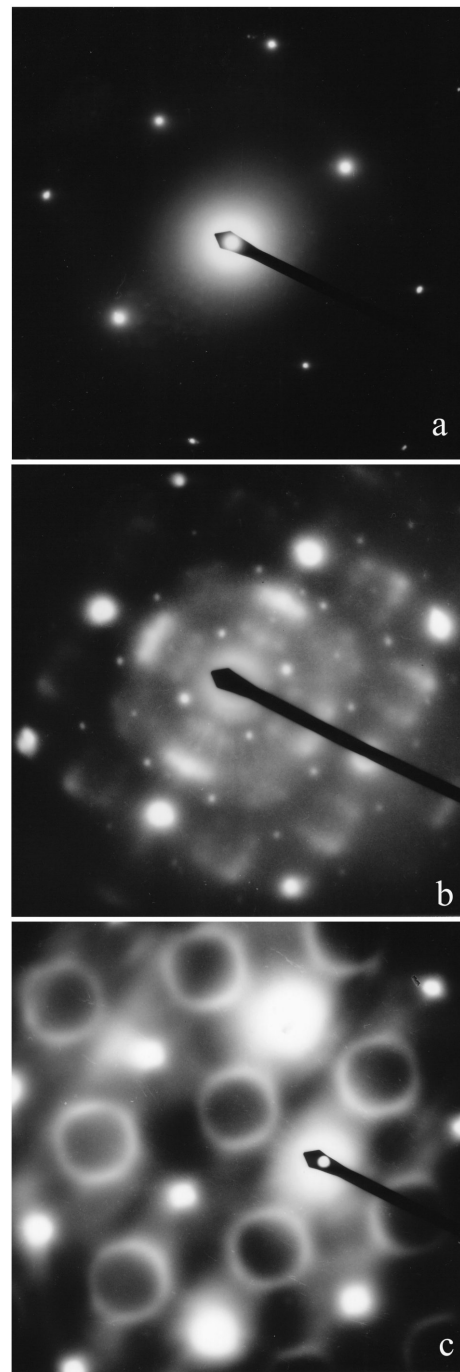


FIGURE 2. (a) Electron diffraction pattern of the compound  $\text{Li}_3\text{NbO}_4$  in the direction  $[001]$ . Only clean and sharp diffraction spots are observed. (b) Electron diffraction pattern of composition  $x = 0.027$  in the direction  $[001]$ . Diffuse scattering is already present at this composition. (c) The diffuse scattering effect is appreciated at increased concentration of cobalt,  $x=0.096$ , and at the same crystal orientation,  $[001]$ , of Fig. 2b.

**a)  $\text{Li}_{(3-3x)}\text{Co}_{4x}\text{Nb}_{(1-x)}\text{O}_4$ ;  $0 < x \leq 0.143$ , at  $850^\circ\text{C}$ .**

A typical X-ray diffraction pattern of the composition region  $0 < x \leq 0.143$  is shown in Fig. 1a. The pattern corresponds to the well known ordered cubic structure of  $\text{Li}_3\text{NbO}_4$  (JCPDS

No. 16-459). A selected area of electron diffraction was used to obtain all diffraction patterns of these compounds. Figure 2a shows a diffraction pattern of  $\text{Li}_3\text{NbO}_4$  ( $x=0$ ) which comprises sharp spots, while in Figs. 2b and c, diffuse intensity is clearly appreciated in the diffraction pattern coming from one crystal fragment of the  $\text{Li}_3\text{NbO}_4$  solid solution at  $x = 0.027$ .

In fact, none of the precursors  $\text{Li}_3\text{NbO}_4$  or  $\text{CoO}$  show any special characteristic in their electron diffraction patterns, which are formed by sharp spots. When compounds of the type  $\text{Li}_{(3-3x)}\text{Co}_{4x}\text{Nb}_{(1-x)}\text{O}_4$  are worked out, then two types of electron diffraction patterns can be recognized, one of them formed by sharp spots, while the other shows diffuse intensity of striking forms accompanying the sharp spots. The amount of small grains which presents diffuse scattering depends on the cobalt concentration as will be discussed later. At very low concentrations, as the one in Fig. 2b, very few grains presenting diffuse scattering were found. Products in this composition interval have a related NaCl-type structure in which oxygen anions and  $\text{Li}^{1+}$ ,  $\text{Nb}^{5+}$ , and  $\text{Co}^{2+}$  cations occur modeling a close packed network. As a matter of fact, we can think that in microscopic regions the participant ions have been set down randomly on the disposal sites in the NaCl-type structure. However, while the phase is being constituted, their final arrangement should be linked with the probability of charge-charge interactions between nearest neighbors, and influenced by the ionic radii as well. The rock salt type structure is illustrated in Fig. 3; here we have drawn octahedral polyhedra locating  $\text{Li}^{1+}$ ,  $\text{Nb}^{5+}$  or  $\text{Co}^{2+}$  ions at the center of gravity of them. There is one vacancy in the octahedron at the center of the cubic cluster, and two more anionic vacancies along the  $c$  direction. The stoichiometry of the cubic cluster is a half of the formula  $\text{Li}_3\text{Co}_2\text{NbO}_6$ .

### b) $0.077 < x \leq 0.272$ , at $1200^\circ\text{C}$ .

The characteristic X-ray pattern of a compound in the composition region  $0.077 < x \leq 0.272$ , which has the feature of

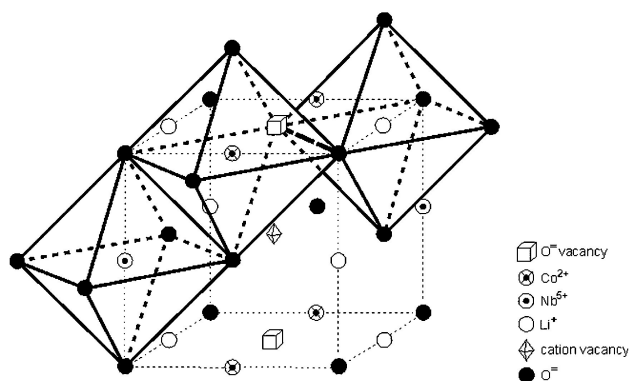


FIGURE 3. The rock salt type structure cluster showing a possible arrangement of octahedral polyhedra locating  $\text{Li}^{1+}$ ,  $\text{Nb}^{5+}$ , or  $\text{Co}^{2+}$  ions at their center of gravity. There is one vacancy in the octahedron at the center of the cubic cluster, and two more anionic vacancies along the  $c$  direction.

being a high temperature phase of  $1200^\circ\text{C}$ , called  $\alpha$  phase, is shown in Fig. 1b. The unit cell was identified as a disordered cubic rock salt phase corresponding to  $\text{CoO}$  (JCPDS No. 9-402). The lattice parameter,  $a$ , in this case is one half ( $\sim 4.2\text{\AA}$ ) of that obtained ( $\sim 8.4\text{\AA}$ ) in the composition interval  $0 < x \leq 0.143$ . In this composition interval, the electron diffraction patterns formed by sharp spots belong to a disordered superstructure of rock salt type. Another class of diffraction patterns comes from a rock salt structure phase, which once again exhibits diffuse scattering characteristics of short range order. Regarding the electron diffraction experiments it was found that, when the  $\text{CoO}$  content increases, a greater and greater percentage of crystallites show diffuse scattering.

In the search of continuously variable solid solutions microscopic crystal changes are frequently possible. In fact, many of the known composition solid solutions phases are found to be modulated either in a long range ordered modulated structure form or in a locally ordered form [9]. If we write modulation wave-vectors as  $\mathbf{q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ , then the only  $\mathbf{q}$  compatible with the requirement

$$\begin{aligned} \delta f\left(\mathbf{T} + \frac{\mathbf{a}}{2}\right) + \delta f\left(\mathbf{T} - \frac{\mathbf{a}}{2}\right) + \delta f\left(\mathbf{T} + \frac{\mathbf{b}}{2}\right) + \delta f\left(\mathbf{T} - \frac{\mathbf{b}}{2}\right) \\ + \delta f\left(\mathbf{T} + \frac{\mathbf{c}}{2}\right) + \delta f\left(\mathbf{T} - \frac{\mathbf{c}}{2}\right) \propto \exp(2\pi i \mathbf{q} \cdot \mathbf{T}) \\ \times \left\{ \cos 2\pi \mathbf{q} \cdot \frac{\mathbf{a}}{2} + \cos 2\pi \mathbf{q} \cdot \frac{\mathbf{b}}{2} + \cos 2\pi \mathbf{q} \cdot \frac{\mathbf{c}}{2} \right\} \end{aligned}$$

for a modulated structure, must satisfy

$$\cos \pi h_1 + \cos \pi h_2 + \cos \pi h_3 = 0.$$

In the former mathematical expression  $\mathbf{T}$  describes a primitive parent unit cell, in the latter  $h_1$ ,  $h_2$ ,  $h_3$  are reciprocal coordinates. Sauvage and Parthé [7] just found this last equation to describe continuous diffuse distribution in sub-stoichiometric solid solutions phases. This represents an appropriate mathematical description of the relations between short range order parameter equations and the diffuse intensity located among Bragg spots. Particularly the treatment has been successfully [10] applied to NaCl related structures. Evidently diffuse intensity is related to a geometric locus. In this last case, the diffuse intensity has to be on a surface described precisely by the equation  $\cos \pi h_1 + \cos \pi h_2 + \cos \pi h_3 = 0$ . This case corresponds to that one where diffuse scattering is concentrated on a shell in the Brillouin zone. We believe that this model can appropriately explain the observed diffuse scattering in the studied  $\text{Li}_{(3-3x)}\text{Co}_{4x}\text{Nb}_{(1-x)}\text{O}_4$  compounds. So, to describe diffuse scattering of the synthesized compounds in terms of this model, we can choose, as the main cluster, a cubic  $fcc$  where the cations are inside the octahedral sites (Fig.3), therefore imagining many possibilities for the  $\text{Li}^{1+}$ ,  $\text{Nb}^{5+}$ , and  $\text{Co}^{2+}$  ions to be distributed in this selected cluster. So, in principle, there is no reason to deny the possibility of atoms entering in short range order ion arrangements to produce the observed

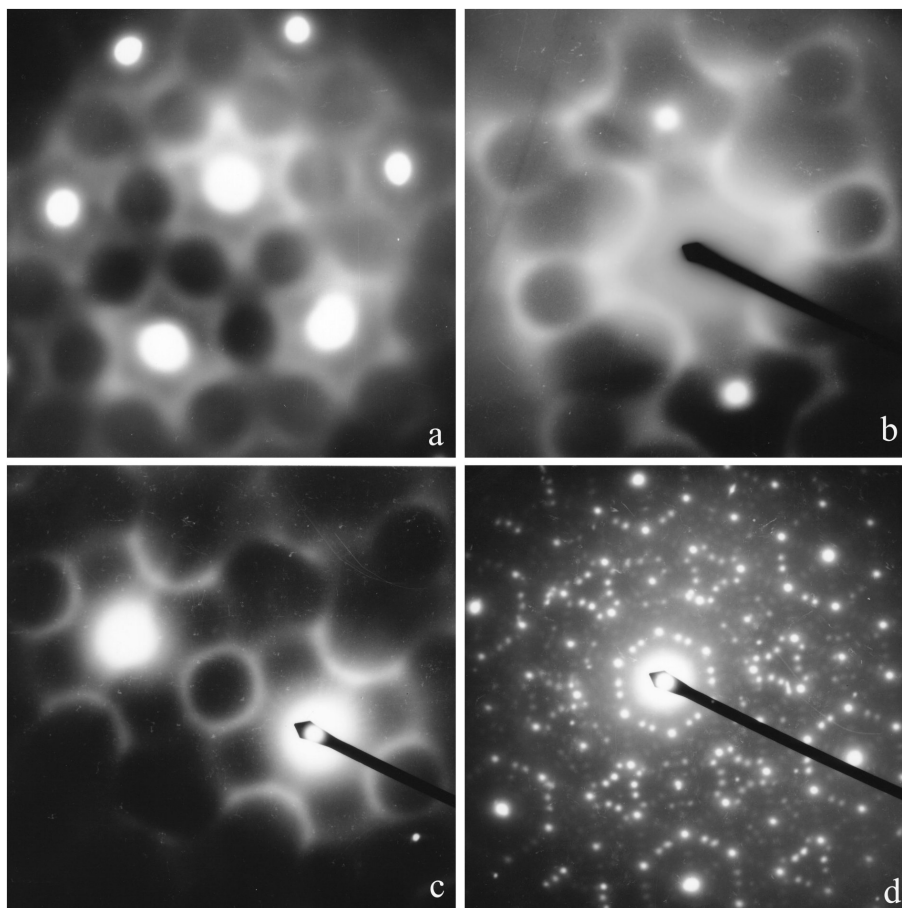


FIGURE 4. At the temperature of 1200°C: (a) In the composition  $x=0.096$  corresponding to  $\alpha$  phase, the diffuse scattering is observed in the direction [111]. (b) and (c) Diffuse electron diffraction of the  $\alpha$  phase at  $x=0.2$  in the directions [013] and [114]. (d) Typical electron diffraction pattern of a transition state of  $\text{Li}_3\text{Co}_2\text{NbO}_6$  in the direction [111].

diffuse scattering. The next point is to explain where the necessary forces which may determine short range order in the structure come from. The origin of short range order seems to be a consequence of the chemical constraint in which local atomic arrangement has a fixed stoichiometry surrounding the column of vacancies aligned along the  $c$  axis.

It seems to be that favorable charge-charge interactions between  $\text{Co}^{2+}$  ions and its surroundings favor the spatial atomic distribution rising to the observed broad diffuse scattering distributed among Bragg spots. This means that in those crystalline grains where diffuse scattering is present, atomic distribution in the lattice produces microscopic ordered domains separated by boundaries constituted by octahedral clusters where  $\text{Li}^{1+}$ ,  $\text{Nb}^{5+}$ , and  $\text{Co}^{2+}$  ions may be randomly placed. Even more, in different crystallites, cations may lay on a different short range arrangement, although what we expect is that the small ordered regions do not necessarily have the same size. The limits between the small regions may from an antiphase grain boundary or other type of complex boundary, whose understanding requires high resolution electron microscopy; this matter falls out of the scope of this research.

In Figs. 4a – c typical electron diffraction characteristics of the composition interval  $0.077 < x \leq 0.272$ , at 1200°C, are shown.

#### c) $x = 0.367$ , $\text{Li}_3\text{Co}_2\text{NbO}_6$

Diffraction electron experiments were made with a sample in the composition  $x = 0.367$ , which is an isostructural phase of  $\text{Li}_3\text{Ni}_2\text{TaO}_6$ , (JCPDS No. 44 - 592), an orthorhombic phase with spatial group  $Fddd$  [11,12], its X-ray diffraction pattern is shown in the Fig. 5. This phase also exhibits diffuse scattering and additional diffraction patterns characteristic of an intermediate stage, as shown in Fig. 4d.

If some special type of reordering occurs in an ordered phase, for example due to thermal energy, the diffuse scattering may lead to sharp spots distributed between the original Bragg spots. This suggests that the structure tends to form a superstructure.

In the samples studied in the above mentioned intervals,  $0 < x \leq 0.143$  and  $0.077 < x \leq 0.272$ , the electron beam does not seem to affect the short range order in the grains when they are under observation, this means that thermal energy from the beam is not enough to activate ion mobility. Hence

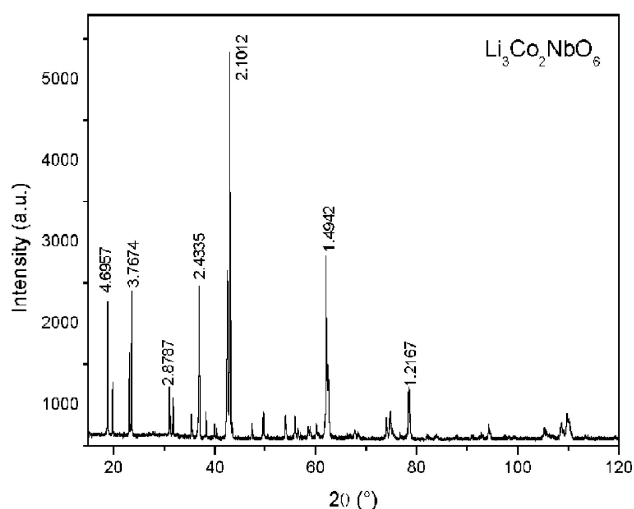


FIGURE 5. X-ray diffraction pattern of the compound  $\text{Li}_3\text{Co}_2\text{NbO}_6$ .

stability of the compounds under the electron beam is quite reasonable. This characteristic is pointed out because the observation of the  $\text{Li}_3\text{Co}_2\text{NbO}_6$  phase in the electron microscope was difficult, the long exposure to the electron beam leads to diffuse intensity becoming zero-dimensional, and at the end the diffraction patterns appear as sharp superstructure spots.

It must be pointed out here that single grains are homogeneous in the sense that, in observing two different regions in a single crystallite, we always found the same type of diffraction pattern.

We must mention that some crystals exhibit diffraction characteristics at an intermediate stage, where no full short range order was established. This means diffraction patterns do not exhibit an arrangement of fundamental spots corre-

sponding to a specific crystal orientation nor a typical short range order effect, as shown in Fig 4.

#### 4. Conclusions

Electron diffraction experiments in the system  $\text{Li}_3\text{NbO}_4\text{-CoO}$  revealed the existence of short range order in their structure. Diffraction features correspond to that of a NaCl type structure. Two types of electron diffraction patterns can be recognized, one of them formed by sharp spots while the other shows diffuse intensity of striking forms, accompanying the sharp spots. Using a cubic cluster model we propose a spatial cation distribution, which include the occurrence of octahedral vacancies, thus giving rise to the observed short range order. The main source of the short range order seems to be the chemical constraint in which local arrangement of cations preserve a fixed stoichiometry surrounding the column of vacancies along of the  $c$  axis. Since in the compound  $\text{Li}_3\text{NbO}_4$  there is no short range arrangements of atoms, then certainly the presence of  $\text{Co}^{2+}$  ions must supply the necessary force to induce appropriate spatial atomic arrangements. On the one hand, the presence of  $\text{Co}^{2+}$  drives local crystal chemistry constraints to the host lattice. On the other hand, the presence of short range order can be interpreted partly as transition states between local order and a superstructure, but also partly as an indication of long range forces associated with the electronic structure.

#### Acknowledgments

We thank Carlos Flores Morales and José Guzmán-Mendoza IIM UNAM for their technical assistance. We thank María Guadalupe Calderón for the editing support. This work was partially supported by the projects DGAPA-UNAM No IN110800 and PAPIIT IN102700 CONACYT 33361-U.

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